

# SYNTHESIS OF COILED CARBON NANOTUBES BY MICROWAVE CHEMICAL VAPOR DEPOSITION

## REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application No. 60/431,888 filed December 6, 2002.

## 5 FIELD OF THE INVENTION

The present invention relates to the field of carbon nanotubes. More particularly, the invention relates to mass-produced coiled carbon nanotubes and to a method for their synthesis using microwave chemical vapor deposition (CVD).

## 10 BACKGROUND OF THE INVENTION

Prior art methods of catalytic chemical vapor deposition (CCVD) have been used to prepare carbon fibers/tubules with different morphologies in different sizes. Among them, fibrous carbon materials with coil morphology have especially attracted a wide interest. This interest relates not only to academic research interests but also to potential versatile commercial applications. Motojima *et al.* first reported regular coiled carbon fibers in micron size by CCVD with thiopene vapor as an impurity gas, named carbon microcoils [Motojima S. *et al.*, "Preperation of coiled carbon fidere by pyrolysis of acetylene using a Ni catalyst and sulfur or phosphorus compound impurity" *Appl. Phys. Lett.* 62 2322-3, 1993]. In this paper, the growth mechanism of carbon microcoils was postulated as resulting from the anisotropic properties of the catalyst for carbon deposition. Such carbon microcoils found applications in EM absorbers, micro springs, etc. Subsequently, Pan *et al.* reported the synthesis of carbon tubule nanocoils using iron-coated indium tin oxide as a catalyst [Pan L. *et al.*, "Growth and density control of carbon tubule nanocoils using catalyst of iron compounds" *J. Mater. Res.* 17 145-8, 2001]. Recently, Varadan *et al.* synthesized carbon nanocoil fibers by using Ni particles [V. K. Varadan, J. Xie, "Synthesis of carbon nanocoils

by microwave CVD" *Smart Materials and Structures*, 11 728-34, 2002]. Such nanocoiled carbon fibers/tubules have been shown to be good candidates for commercial applications, especially field emission display technology [Pan L. *et al.*, "Field emission properties of carbon tubule nanocoils" *Jpn. J. Appl. Phys.* 40 L235-7, 2001]. Note that all of the coiled carbon fibers/tubules mentioned above are prepared using amorphous carbon materials.

In contrast to the conventional method of producing carbon nanocoils, the present invention relates to coiled carbon nanotubes. Since the discovery of carbon nanotubes by Iijima, coiled carbon nanotubes have become objects of widespread interest. The primary difference between coiled carbon nanotubes and carbon nanocoils lies in the crystalline graphitic structures of the nanotubes. Also, the diameter of coiled carbon nanotubes (<100 nm) is much smaller than the diameter of carbon nanocoils. The coil morphology, together with as well as the extraordinary properties of nanotubes, make coiled carbon nanotubes a promising material for hydrogen storage, field emission, EM absorber and nanotechnology applications in general.

Nanotubes prepared from CCVD methods tend to be produced in straight or randomly curled morphologies. For example, accidentally coiled carbon nanotubes were reported in extremely low yield by Hernadi *et al.* ["Fe-catalyzed carbon nanotube formation" *Carbon* 34 1249-57, 1996]. Also, Amelinckx *et al.* reported a formation mechanism for catalytically grown helix-shaped graphite nanotubes ["A formation mechanism for catalytically grown helix-shaped graphite nanotubes" *Science* 265 635-9, 1994]. According to their results, the coil morphology of carbon nanotubes is due to the mismatch between the extrusion velocity and the rate of carbon deposition.

Thus far the synthesis of coiled CNT has been reported as a byproduct of regular CNT synthesis. It would be more accurate to say that coiled CNTs have been found under microscope by accident because there was no control for the synthesis of coiled CNT. To date, neither specific process conditions nor special catalyst compositions have been identified for the effective and consistent synthesis of coiled CNTs. Despite the early indications of the usefulness of coiled CNTs, there continues to be a strong need for the effective synthesis of regular coiled carbon nanotubes.

CNTs, along with coiled carbon nanotubes, are the most promising materials anticipated to impact future nanoscience and nanotechnology. Their unique structural and

electronic properties have generated great interest for use in a broad range of nanodevices. A significant amount of work has been done in the past decade to reveal the unique structural, electrical, mechanical, electromechanical and chemical properties of carbon nanotubes and to explore the key applications of this novel material. Most of these applications will require efficient fabrication methods capable of producing pure CNTs, including coiled carbon nanotubes, to meet device requirements. Another advantage of coiled carbon nanotubes is that they are capable of forming in situ semiconductor-metallic or semiconductor-insulator junctions which one can utilize for the fabrication of nanodevices. Coiled carbon nanotubes also have an greater surface area than CNTS which increases their functionalization. Accordingly it is an object of the present invention to provide effective and efficient methods of fabricating CNTs, especially coiled carbon nanotubes, to enable the commercialization of applications using such.

### **SUMMARY OF THE INVENTION**

The invention is a method for synthesizing coiled carbon nanotubes using a microwave CVD system with inventive processing conditions and specialized catalyst(s). Preferred conditions include the use of acetylene as a hydrocarbon source gas in a microwave CVD system without using an impurity gas and using an iron supported on magnesium carbonate as a catalyst. The invention also includes the resulting coiled carbon nanotubes.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows a schematic diagram of a conventional thermal filament CVD system.

Figure 2 shows a schematic diagram of a microwave CVD system used in the present invention.

Figure 3 shows an illustration of a coiled carbon nanotube.

Figure 4 shows a flow diagram for the flow control systems.

Figure 5 shows a SEM micrograph of coiled nanotube synthesized using a microwave CVD system in accordance with the present invention.

Figure 6 shows a TEM image of coiled nanotubes obtained from a microwave CVD system in accordance with the present invention.

### **DETAILED DESCRIPTION OF THE INVENTION**

Referring now to FIG. 1, an apparatus designed to perform this method is designated in its entirety by the reference numeral 8. The method generally involves placing a catalyst 3 inside of a reaction chamber 1 and then heating up the reaction chamber 1. In one embodiment of the method, a quartz reaction tube 2 is used to transport the catalyst in and out of the reaction chamber 1. The temperature is monitored by a thermocouple 7. When the temperature inside has reached a certain level (usually 700°C) a hydrocarbon source gas 4 (such as acetylene) is pumped into the reaction chamber 1 through a intake valve. The hydrocarbon source gas 4 is then broken down into its elements which interact with the catalyst 3 resulting in the growth of carbon nanotubes. The exhaust gas 6 is removed from the reaction chamber 1. In one embodiment of this method, argon 5 is pumped into the reaction chamber 1 for purging.

FIG. 2 shows a microwave CVD system 9 according to a preferred embodiment of the present invention. Until now, this method has involved the use of a furnace to heat the reaction chamber 33. The present invention uses a magnetron 10 in place of a furnace. Although a magnetron 10 capable of producing 750 W is preferred, any commercially-available magnetron may be used. The magnetron 10 creates a microwave field inside the reaction chamber 33.

In the preferred method of the invention, a known amount of the catalyst and catalyst support 15 are dispersed onto the substrate 34. The substrate 34 is then loaded into the reaction chamber 33. In this embodiment, the substrate 34 is loaded in and out of the reaction chamber 33 in a quartz container 19. The magnetron 10 is then switched on to heat the substrate 34 to the reaction temperature. In this embodiment, the reaction temperature is set to 700°C. During heating, an inert gas 22, at an optimized flow rate, can be used for purging, although the use of an inert gas 22 is not required for the present invention. When the reaction temperature is reached, a hydrocarbon source gas 21 is introduced into the reaction chamber at an optimal flow rate. The gases are pumped into the reaction chamber 33 through the gas inlet 17 and blown onto the substrate 34 using a quartz gas distributor 16.

Exhaust gas leaves the chamber through the gas outlet 18. In this embodiment the reaction is set to 30 minutes. After the reaction, the resulting product is scratched from the substrate. Previous experiments by Varadan, V. *et al.* ["Synthesis of carbon nanocoils by microwave CVD" *Smart. Mater. Struct.* 11 (2002) 728-734] did not involve the production of carbon nanocoils, and utilized different processing materials and conditions than described in the present invention.

The advantage of using a microwave field is that it is uniform throughout the reaction chamber 33. This uniform field allows for a higher quantity of coiled carbon nanotubes with consistent properties to be produced during each reaction. In addition, a microwave field can be instantly turned off whereas a reaction chamber heated by a furnace must be allowed to cool to room temperature before any nanotubes can be extracted. This dramatically reduces the lag time between production rounds. In the preferred embodiment of the invention, a commercially available stub tuner 12 is used prevent any reflected power from flowing into the magnetron 10. In one example, the inventors manually adjusted the stub tuner 12. In another example, a commercially available three-port circulator 13 was used to automatically adjust the stub tuner 12. In addition, the invention may comprise a circulating chiller 14 which cools the magnetron 10 and therefore extends its life. The invention may further comprise a stirrer 27, which assists in making the microwave field uniform. The stirrer 27 is driven by a motor 28.

The reaction chamber 33 can be made from any number of materials without departing from the scope of the present invention. For instance, in one embodiment the reaction chamber is constructed out of aluminum. In a further embodiment, the reaction chamber is made of steel. In the preferred embodiment, the reaction chamber is a cylinder. The inventors used two reaction chambers manufactured by HVS Technologies. The smaller reaction chamber had dimensions of 14" in length and 5.75" in diameter. The larger reaction chamber had dimensions of 70" in length and 35" in diameter.

Although the catalyst can be made from various materials without departing from the scope of the present invention, a preferred catalyst is iron. Iron is preferred because it produces the highest yield of coiled carbon nanotubes. Alternatively, other transition metal catalysts can be used; including combinations of transition metals (*e.g.*, bimetallic catalysts). It is important to note here that the indium-tin-iron catalyst disclosed in U.S. Pat. No.

6,583,085 to Nakayama *et al.* is not preferred for this invention. The presence of tin in the catalyst would cause the catalyst to spark when placed in the microwave field. In addition, the indium-tin-iron catalyst would not be preferred does not easily absorb the microwaves.

5 The specific support used in the method of the present invention is critical. The support must contain pores giving rise to the growth of coiled carbon nanotubes according to the invention as opposed to other formations, such as fibers. The supports must also be able to easily absorb microwaves. Some non-limiting examples include silica, zeolite, and magnesium carbonate (preferred). Preferred pore sizes lie in the range of 0.1 to 10 nm with a surface area of 250-300 m<sup>2</sup>/g. The following are three examples of catalyst supports and  
10 catalysts with which they were combined (being just three examples of “supported metal catalyst”).

### **EXAMPLES**

#### **15 Catalyst and Catalyst Support #1**

Iron nitrate and magnesium carbonate were weighed 1:1 weight ratio. Iron nitrate was dissolved in water and the resulting solution was added to magnesium carbonate, followed by continuous stirring to obtain a semi-solid mixture. The semi-solid mixture was kept inside an overnight at 500°C. After allowing the mixture to cool to room temperature,  
20 the resulting brown color solid was powdered. While the pore size of the magnesium carbonated varied somewhat throughout its surface, a majority were 10 nm in diameter.

#### **Catalyst and Catalyst Support #2**

25 Iron nitrate and silica were weighed 1:1 weight ratio. Iron nitrate was dissolved in water and the resulting solution was added to silica, followed by continuous stirring to obtain a semi-solid mixture. The semi-solid mixture was kept inside an oven at 120°C overnight. After allowing the mixture to cool to room temperature, the resulting brown color solid was powdered. As a porous substance, the pore sizes for silica varied throughout its length.

### Catalyst and Catalyst Support #3

The inventors used "hydrothermal processing" to manufacture zeolite (although commercial grade zeolite may be used). The hydrothermal processing method is described in Cundy, C. *et al.* ["The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time" *Chem. Rev.* 2003, 103, 663-701] Nickel acetate was dissolved in water and a proper amount of zeolite was added into the solution with a Ni percentage in zeolite of 14.5wt%. The gel solution was stirred and kept in an oven at 120°C overnight. After drying, the solid was crushed into a fine powder. While the pore size for zeolite varied throughout its surface, the majority were 1 nm in diameter.

The substrate **34** is made of silicon carbide. Although the hydrocarbon source gas **21** can be any gas containing carbon, in the preferred embodiment the hydrocarbon source gas is acetylene. The inventors found that the optimal flow rate for acetylene is 30 sccm for the smaller reaction chamber (14" × 5.75") and 600 sccm for the larger one (70" × 35"). Other non-limiting examples include methane, ethane and propane.

When an inert gas **22** is also used as described herein, helium is preferred, although any inert gas can be used (such as argon). The inventors found the optimal flow rate for helium is 190 sccm for the smaller reaction chamber and 3500 sccm for the larger one. It is important to mention here that for the synthesis of coiled carbon nanotubes by a conventional CCVD method, the presence of an impurity gas (e.g. thiophene) is necessary, while in the microwave CVD method, no impurity gas is required.

To optimize the processing conditions, the temperature of the reaction chamber **33** and the gas flow rates can be monitored by a computer **26**. FIG. 4 is a software flow chart for the flow control systems. The temperature of the reaction chamber **33** is monitored by a pyrometer **23**, which in the preferred embodiment is an optical pyrometer **25**. The temperature readings taken by the pyrometer **23** are transmitted to a computer **26**. The computer **26** then compares the temperature of the reaction chamber **33** with the set temperature for processing (preferably 700°C). The computer **26** then controls the switching power supply **11** which in turn controls the magnetron **10**. If the reaction chamber temperature is too low, the computer **26** will tell the switching power supply **11** to turn on the magnetron **10** and increase the temperature. If the reaction chamber temperature is too low,

the computer 26 will tell the switching power supply 11 to turn off the magnetron 10. The computer 26 also communicates with the master flow controller 20 which controls the mass flow controllers 24. The mass flow controllers 24 control the flow rates of the inert 22 and hydrocarbon source gas 21.

5 An illustration of a coiled carbon nanotube is shown in FIG. 3. The distance between the coils is substantially uniform throughout the length of each coiled carbon nanotube. In addition, the diameter of each coiled carbon nanotube will also be substantially uniform. The coiled carbon nanotube 29 is composed of carbon rings in the shapes of pentagons 32, hexagons 30, and heptagons 31. Depositing the various shapes in specific locations along the  
10 surface of the carbon nanotube causes the carbon nanotube to assume a coiled shape. Depending upon the distance between the coils, the non-hexagonal/hexagonal ratio of the carbon rings ranges from 0.1:1 to 1:1. A non-hexagonal/hexagonal ratio of 0.1 produces a "loose" coil with a large pitch. A non-hexagonal/hexagonal ratio of 1:1 produces a "tight" coil with a small pitch. The exact morphology of coiled carbon nanotubes will depend on the  
15 catalyst/catalyst support that is used and the conditions of the microwave CVD.

A scanning electron microscope (SEM 3000N manufactured by Hitachi) was used to investigate the morphology of the coiled carbon nanotubes. Due to the conducting property of carbon nanotubes, no gold coating is necessary for SEM operation. A transmission electron microscope (TEM 420T manufactured by Philips) was used to study the  
20 nanostructure of the coiled carbon nanotubes. TEM samples were prepared by ultrasonic vibration of a small amount of material in acetone followed by dropping on a TEM grid (Lacey carbon film on 300 mesh copper grid, Electron Microscopy Science).

In the SEM micrograph shown in FIG. 5, the coiled morphology for the microwave CVD samples is clearly revealed. From the TEM micrograph shown in FIG. 6, the hollow  
25 structure as well as coiled morphology for the microwave CVD samples was confirmed.

Under optimized conditions, the inventors have achieved ~90% yield of coiled carbon nanotubes. While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various alterations in form and detail may be made therein without departing from the  
30 spirit and scope of the invention. In particular, the particular metal catalysts, supports, source



gas, and flow rates used can vary significantly and still be within the optimization scope of the present invention.